Molecular Dynamics calculation of diffusion in liquid Lithium

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Molecular Dynamics is a computer experiment

The MD method calculates the physical properties of a system by using the classical equations of motion (EOM) that are numerically solved on a computer. Therefore, it computes the phase space trajectories of a collection of "particles" that individually obey classical laws of motion.

As the EOM are approximated by a suitable scheme, there will be an error involved due to transformation of continuous equations to discrete ones but it could be made as small as desired, depending on the needs.

After an initial relaxation stage, thermodynamic variables of the system could be obtained by using averaging over the trajectories.

$$\overline{A} = \lim_{t' \to \infty} \frac{1}{(t' - t_0)} \int_{t_0}^{t'} A(r^N(t), p^N(t); V(t)) dt,$$

$$\overline{A} = \langle A \rangle_{NVE}.$$

The MD results are as good as the inter-particle potential functions are. In this presentation we compared the Lithium and Helium diffusion coefficients for three Li-Li potential functions.

We also show our future plans for MD simulation of bubble formation in liquid Lithium under irradiation by plasma particles and calculation of sputtering yield, due to a bubble blasting and/or splashing.

Li-Li, He-He, and Li-He potential functions

A tight-Binding approximation of quantum mechanics (see formula 1) was used in Ref.[1] for obtaining a suitable ion-ion potential for disordered Lithium system (small clusters). He-He potential was chosen of (exp-6) type. Li-He potential was obtained by a geometry rule.

$$(\varepsilon_{ia}^{0} - E)\,|ia\rangle + \sum_{j \neq i}\sum_{b} t_{ab}^{ij}(r_{ij})\,|ib\rangle = 0, \quad (1)$$

$$U_{coh} = U_{el} + U_{rep},$$

$$U_{rep} = \sum_{i} \varepsilon_0 \sum_{j \neq i} \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right],$$

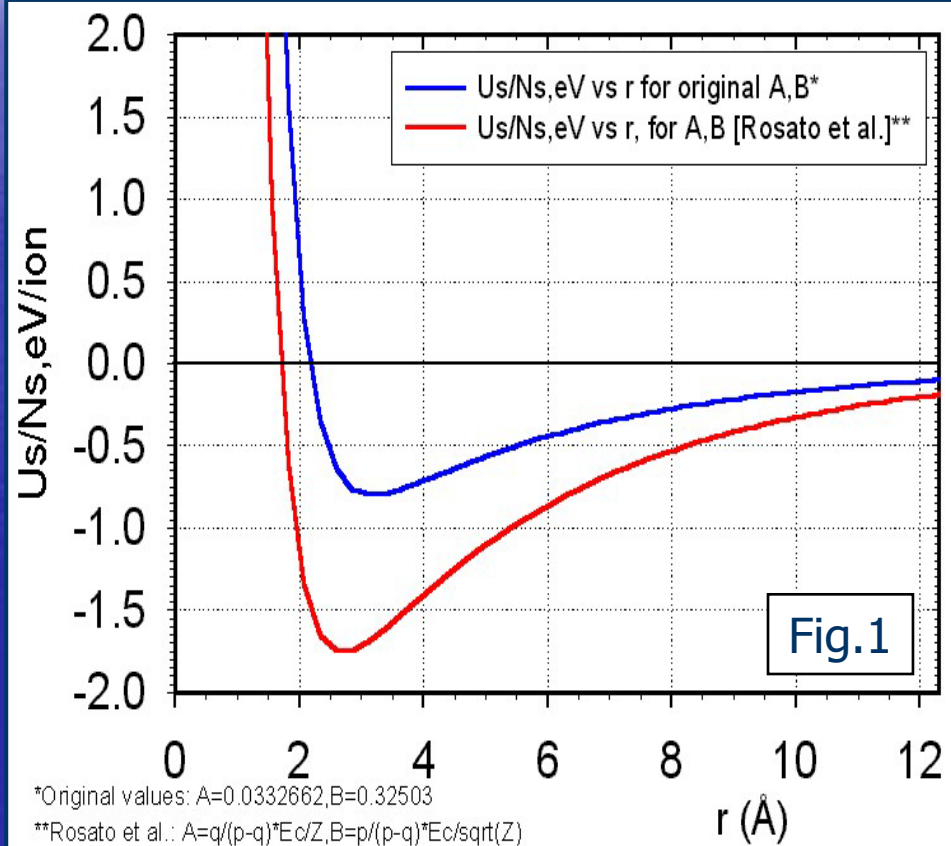$$U_{el} = -\sum_{i}\left\{\sum_{j \neq i} \varsigma_0^{2} \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right]\right\}^{1/2}$$

Parameters used for this simulation:

	ε_0, mRy	ς_0, mRy	p	q	r_0, a.u.
Li-Li:	2.4450	23.889	7.75	0.737	5.490
He-He:	0.735		14.5		5.21
Li-He:	0.735		14.0		5.35

Reference:
[1] Y.Li, E.Blaisten-Barojas, D.A.Papaconstantopoulos Phys. Rev. B57 (1998) pp.15519-15532.

Fig.1

*Original values: A=0.0332662,B=0.32503
**Rosato et al.: A=q/(p-q)*Ec/Z,B=p/(p-q)*Ec/sqrt(Z)

Li-Li potential

In [2,3], an inter-ionic potential for liquid Lithium was obtained and tabulated for five temperature and density points that are located near the Lithium experimental melting line [1], as it is shown in Fig.2. We used a cubic spline, for both the energy and the forces, to calculate the Li self-diffusion coefficient.

Fig.2
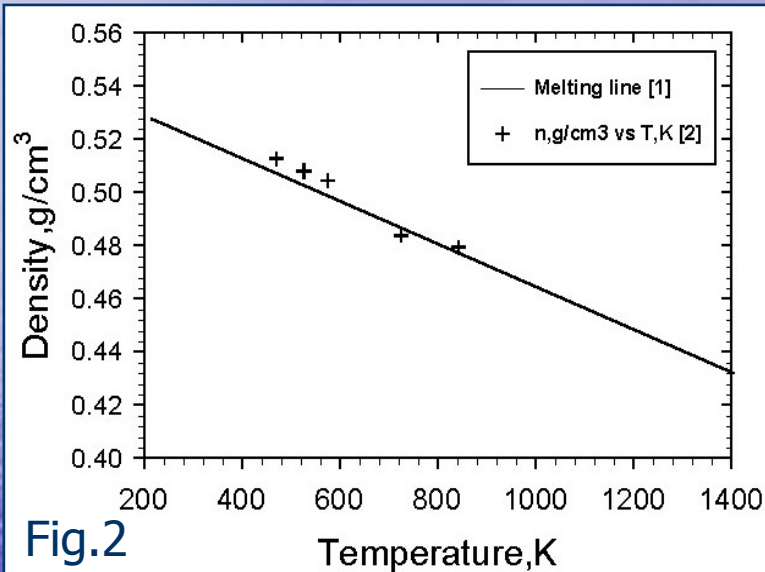
Fig.3

References:
[1] H.Morimoto, S.Kamei, A.Mizuno, T.Itami, to be published.
[2] M.Canales, J.A.Padro, L.E.Gonzalez, A.Giro J.Phys.: Cond.Matt. 5 (1993) pp.3095-3102.
[3] M.Canales, L.E.Gonzalez, J.A.Padro, Phys.Rev. E50 (1994) pp.3656-3669.
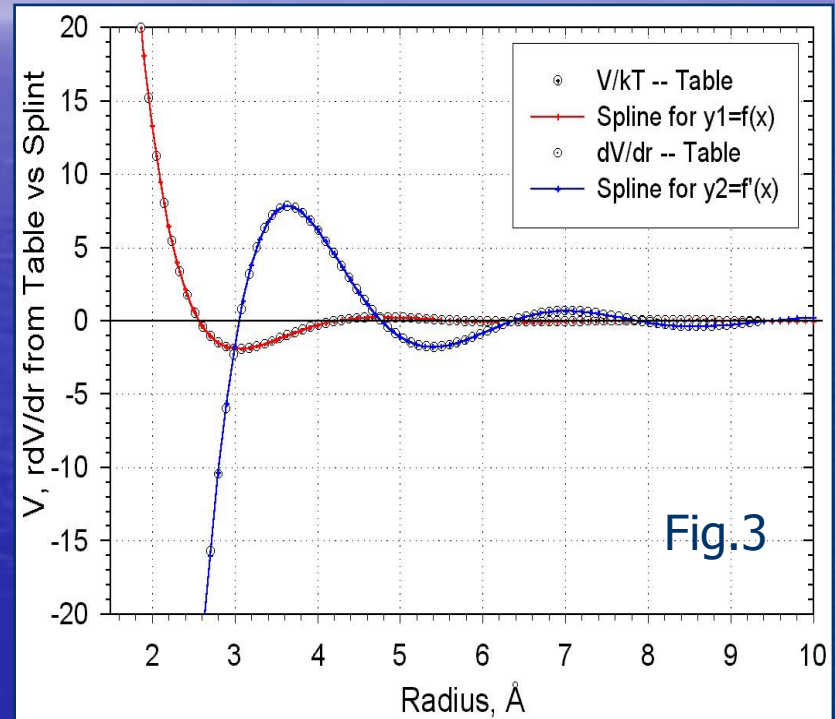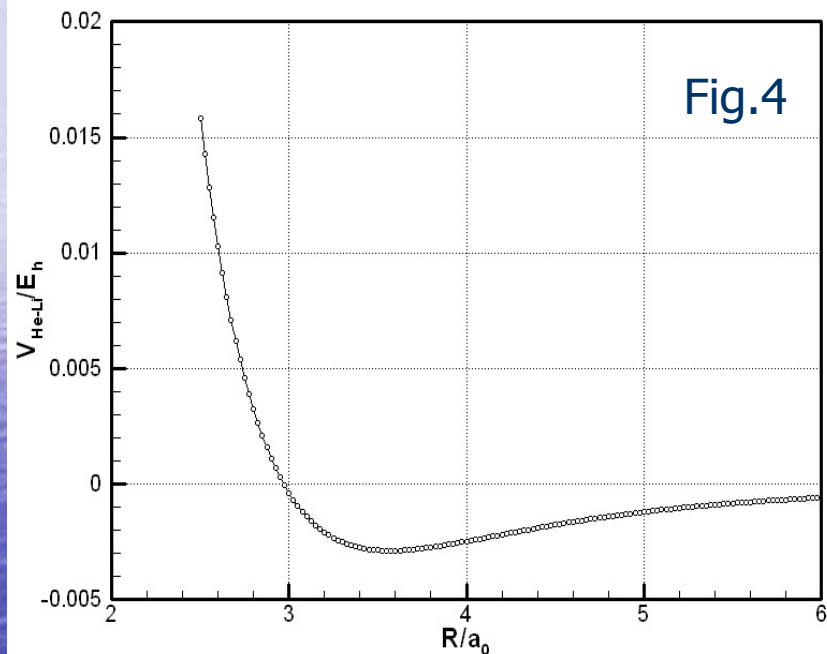
The above Fig.3 compares the tabulated potential and its first derivative given in [2,3] (circles) with the cubic spline (red and blue lines) used in our present work.

He-Li potential

In [1], a He-Li potential function was obtained, as it is shown in Fig.4. We used a cubic spline, for both energy and forces, to calculate the Li self-diffusion coefficient.

Fig.4

Atomic units: Distance $a_0 = 0.529\text{Å}$, Energy $E_h = 27.2\text{eV}$,

References:
[1] P.Soldan et al., Chem.Rev.Lett. 343 (2001) 429-436.
[a] D.M. Bishop, J. Pipin, Chem.Rev.Lett. 236 (1995) 15.
[b] R.Ahlrichs, H.J. Böhm, S. Brode, K.T. Tang, J.P. Toennies, J. Chem.Phys. 88 (1988) 6290.

Evaluation of forces for the He-Li potential from Ref [1].

$$V_{rep}(R) = A\exp(-bR), \quad V_{atr}(R) = -\sum f_n(R)\frac{D_n}{R^n}, \quad (n=4,6,7,8)$$

$$f_n(R) = 1 - \exp(-bR)\sum_{k=0}^{n}\frac{[bR]^k}{k!},$$

$$A = 20.8682, \quad b = 2.554, \quad D_4 = \alpha_1/2, \quad D_6 = \alpha_2/2 + C_6, \quad D_7 = -B/2,$$

$$D_8 = \alpha_3/2 + \gamma/24 + C_8,$$

$$\alpha_1 = 1.383192^a, \quad \alpha_2 = 2.4451^a, \quad \alpha_3 = 10.6204^a, \quad \gamma = 43.104^a,$$

$$B = -7.3267^a, \quad C_6 = 0.298^b, \quad C_8 = 1.98^b.$$

$$F_r = -\frac{\partial V_{tot}}{\partial r} = -\left(\frac{\partial V_{rep}}{\partial r} + \frac{\partial V_{atr}}{\partial r}\right),$$

$$\left(\frac{\partial V_{rep}}{\partial r}\right) = -Abe^{-bR}.$$

$$f_4(R) = 1 - e^{-bR}\left[1 + \frac{bR}{1!} + \frac{(bR)^2}{2!} + \frac{(bR)^3}{3!} + \frac{(bR)^4}{4!}\right],$$

$$f_6(R) = f_4(R) - e^{-bR}\left[\frac{(bR)^5}{5!} + \frac{(bR)^6}{6!}\right],$$

$$f_7(R) = f_6(R) - e^{-bR}\left[\frac{(bR)^7}{7!}\right],$$

$$f_8(R) = f_7(R) - e^{-bR}\left[\frac{(bR)^8}{8!}\right],$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=4} = f_4'(R)\frac{D_4}{R^4} - 4f_4\frac{D_4}{R^5},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=6} = f_6'(R)\frac{D_6}{R^6} - 6f_6\frac{D_6}{R^7},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=7} = f_7'(R)\frac{D_7}{R^7} - 7f_7\frac{D_7}{R^8},$$

$$-\left(\frac{\partial V_{atr}}{\partial r}\right)_{n=8} = f_8'(R)\frac{D_8}{R^8} - 8f_8\frac{D_8}{R^9}.$$
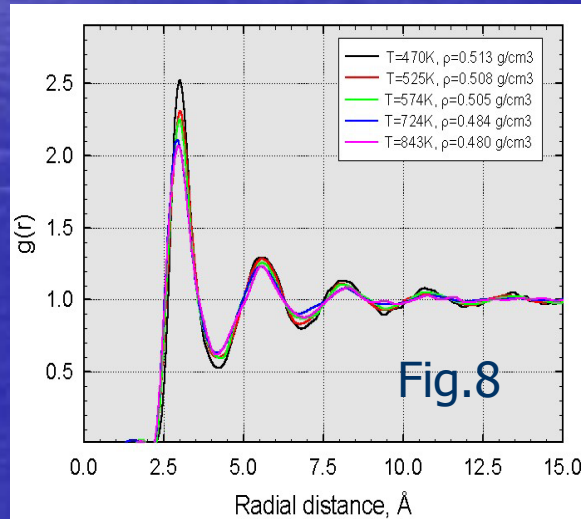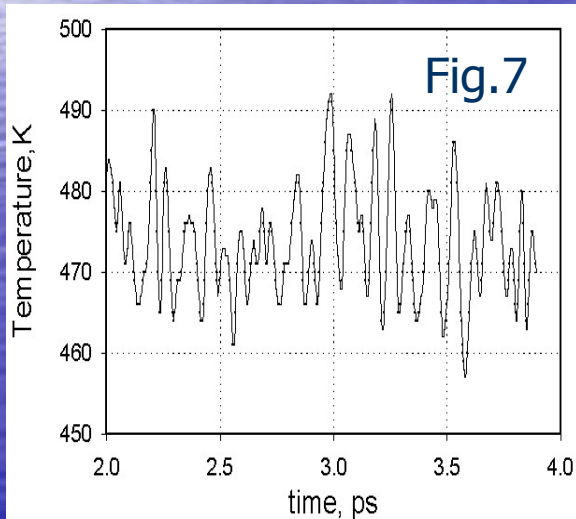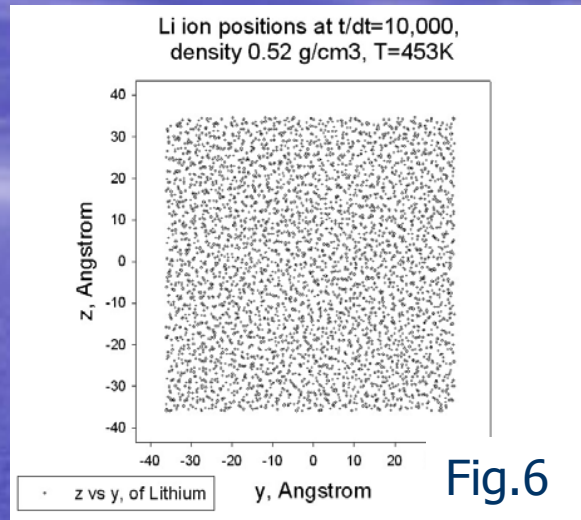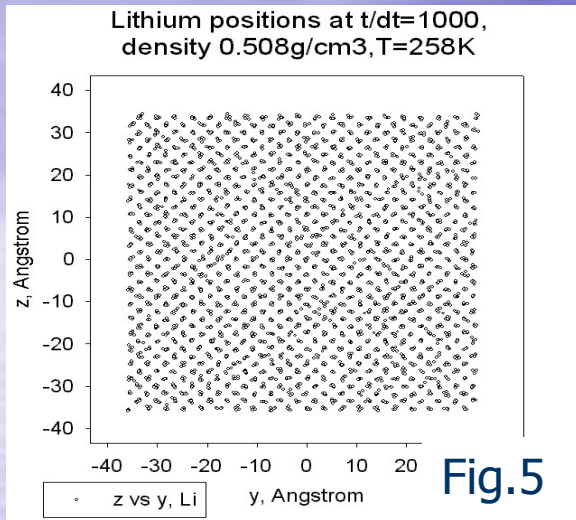
$$f_4'(R) = be^{-bR}\left[\frac{(bR)^4}{4!}\right],$$

$$f_6'(R) = f_4'(R) + be^{-bR}\left[\frac{(bR)^6}{6!} - \frac{(bR)^4}{4!}\right],$$

$$f_7'(R) = f_6'(R) + be^{-bR}\left[\frac{(bR)^7}{7!} - \frac{(bR)^6}{6!}\right],$$

$$f_8'(R) = f_7'(R) + be^{-bR}\left[\frac{(bR)^8}{8!} - \frac{(bR)^7}{7!}\right],$$

Structure of liquid Lithium

Lithium positions at t/dt=1000,
density 0.508g/cm3,T=258K

Fig.5

Li ion positions at t/dt=10,000,
density 0.52 g/cm3, T=453K

Fig.6

Fig.7

Fig.8

Liquid Lithium structure was prepared as follows. We started from an ideal lattice (Fig.5), then it was melted (Fig.6) by heating at a high temperature for 30,000 time steps. After that the liquid was equilibrated for 10,000 time steps and then the physical variables were obtained: the system temperature (Fig.7), the radial distribution function (Fig.8), the velocity-autocorrelation function (vacf) (Fig.9), as an average for 20,000 time steps.

Melting and diffusion in liquid lithium
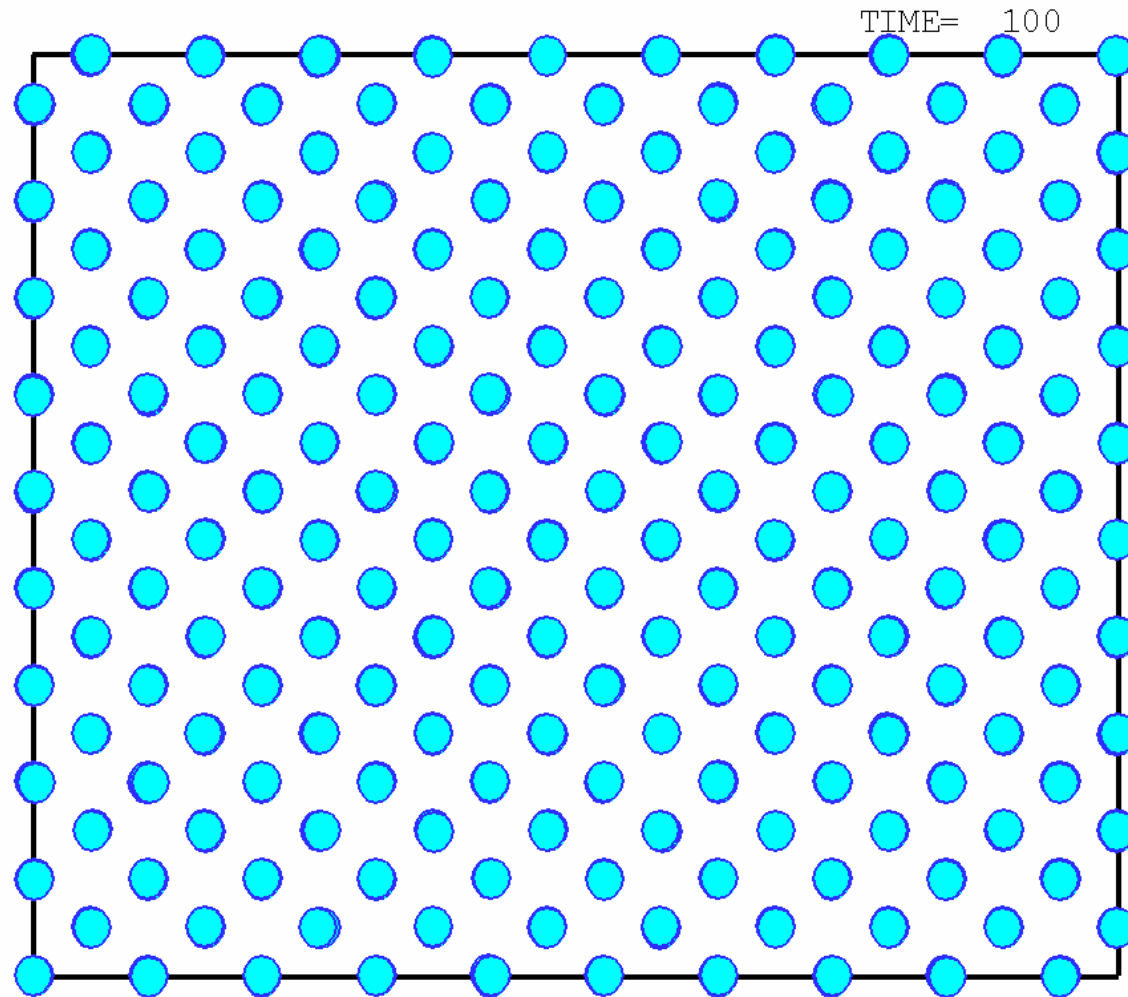
Diffusion coefficient by MD

The Li self-diffusion coefficient was obtained by two methods: as a tangent of the ionic mean-square-displacements (Fig.9) and as a Fourier-transform of the vacf(t) (Fig.10).
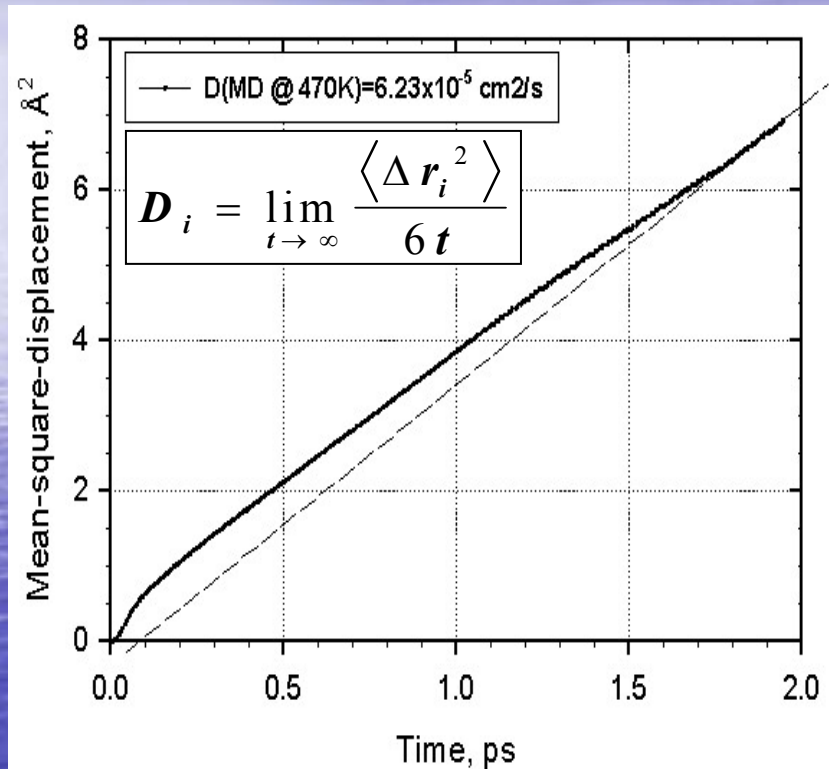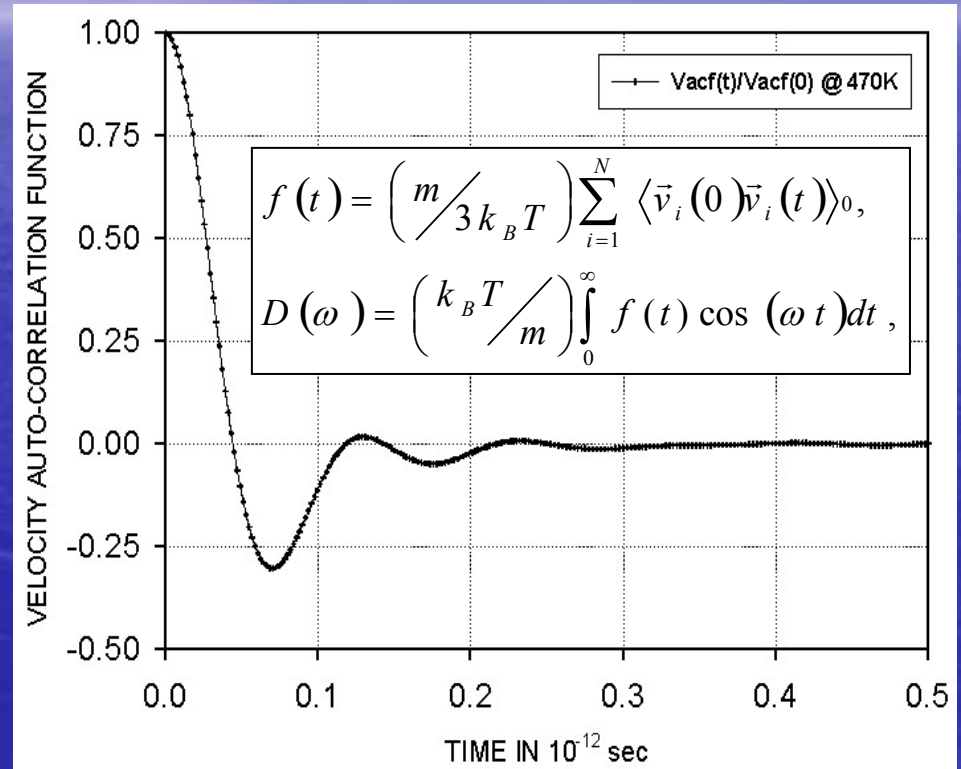

$$D_i = \lim_{t \to \infty} \frac{\langle \Delta r_i^2 \rangle}{6t}$$

D(MD @ 470K)=6.23x10^{-5} cm2/s

Fig.9

$$f(t) = \left(\frac{m}{3 k_B T} \right) \sum_{i=1}^{N} \langle \vec{v}_i(0) \vec{v}_i(t) \rangle_0 ,$$

$$D(\omega) = \left(\frac{k_B T}{m} \right) \int_0^\infty f(t) \cos(\omega t) dt ,$$
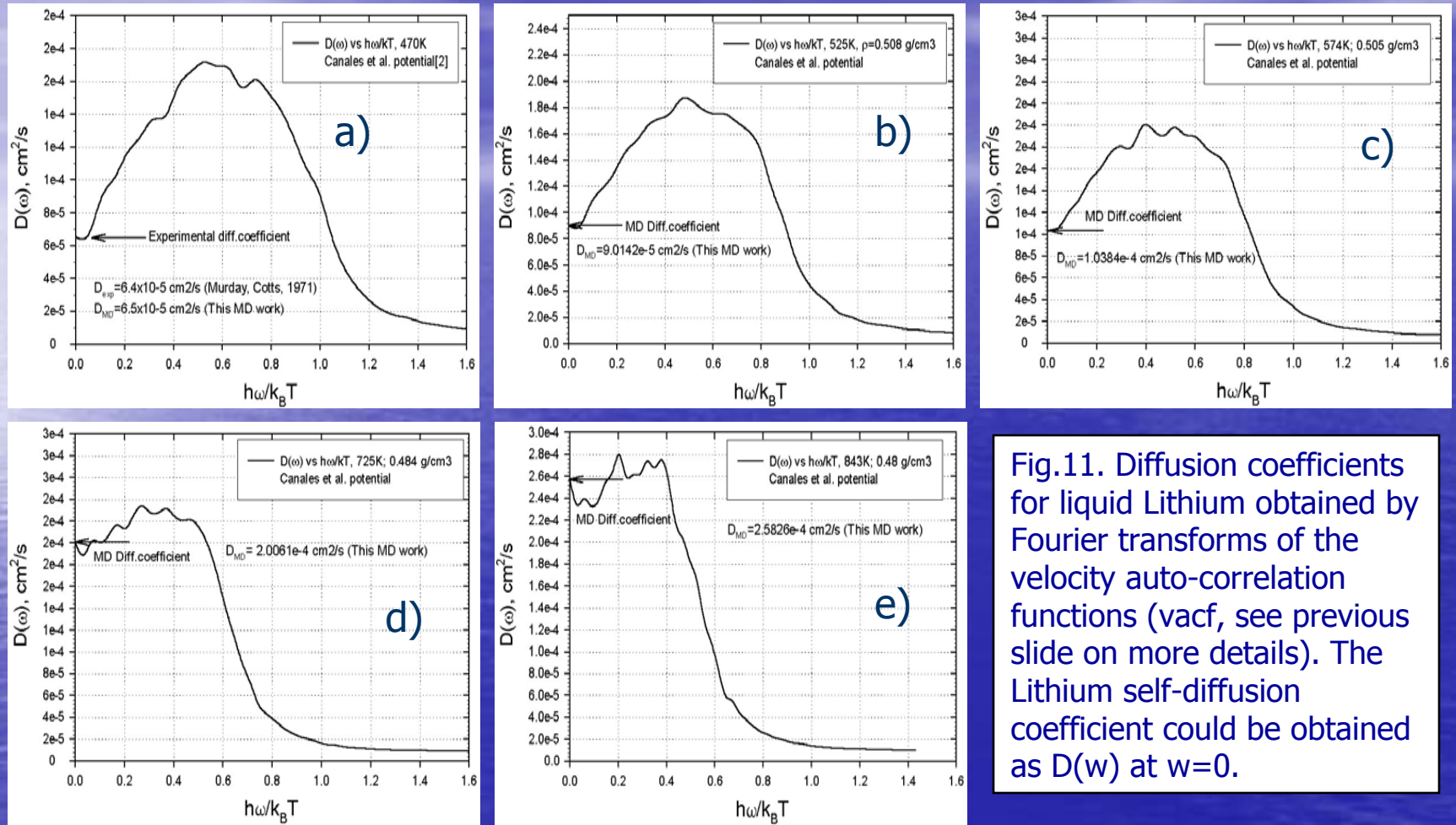
Vacf(t)/Vacf(0) @ 470K

Fig.10

Fig.11. Diffusion coefficients for liquid Lithium obtained by Fourier transforms of the velocity auto-correlation functions (vacf, see previous slide on more details). The Lithium self-diffusion coefficient could be obtained as D(w) at w=0.

The temperature and densities used for the above figures correspond to those data points at which there exist an inter-ionic potential: a) T=470K, density 0.513 g/cm3; b) T=525K, density of 0.508 g/cm3; c) T=574K, density 0.505 g/cm3; d) T=725K, density 0.484 g/cm3; e) T=843K, density 0.48 g/cm3.

Trajectories of diffusing particles
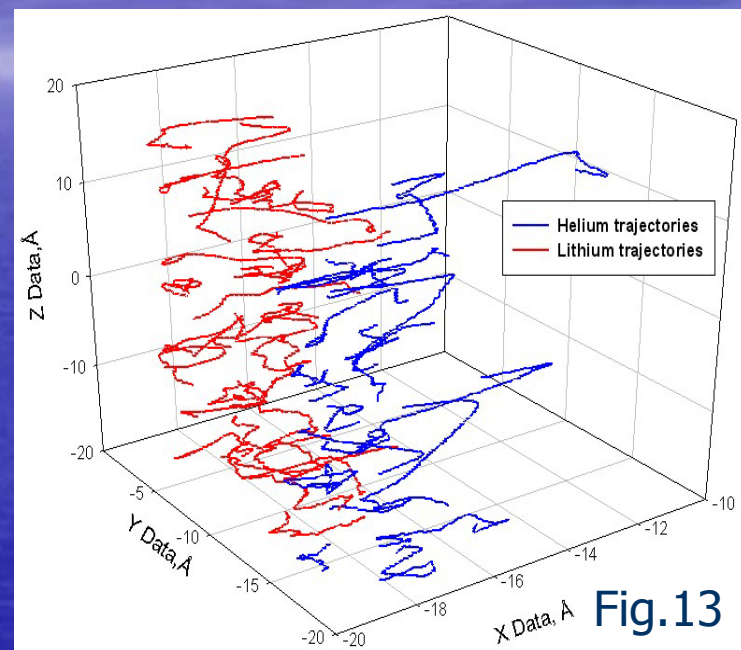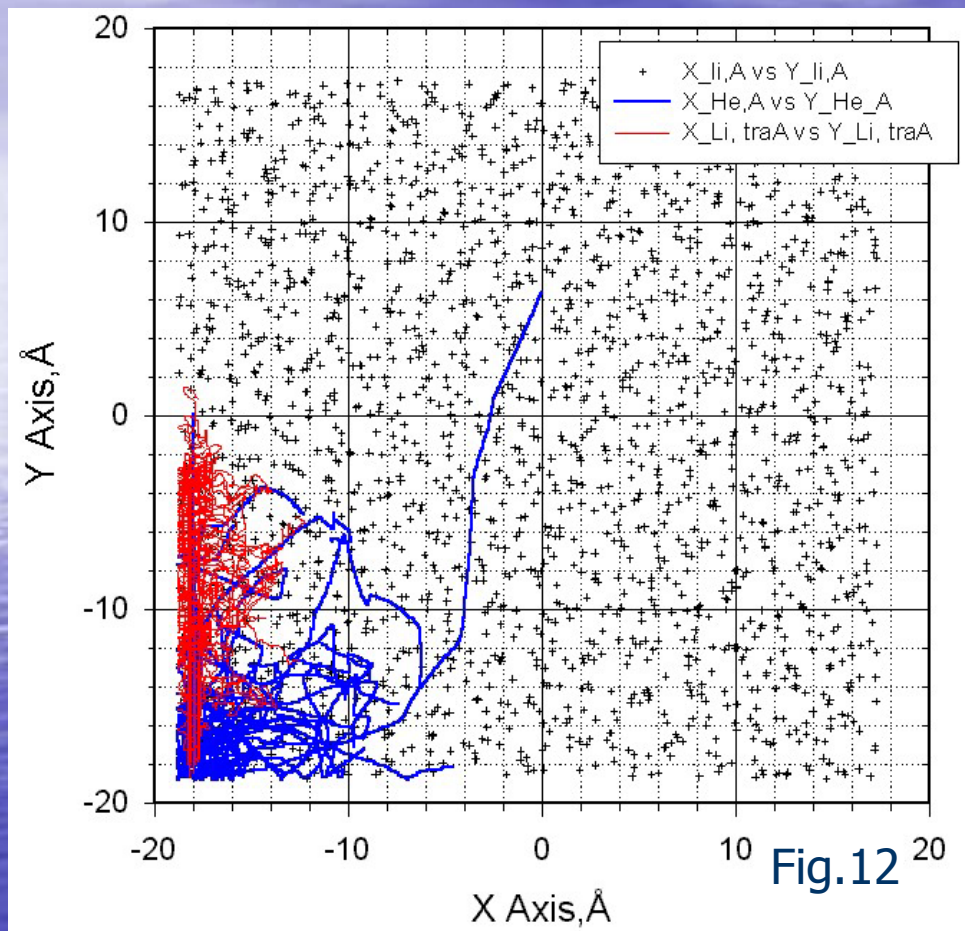

Fig.12

Fig.13

Fig.12-13. The blue lines are the trajectories for Helium atoms.

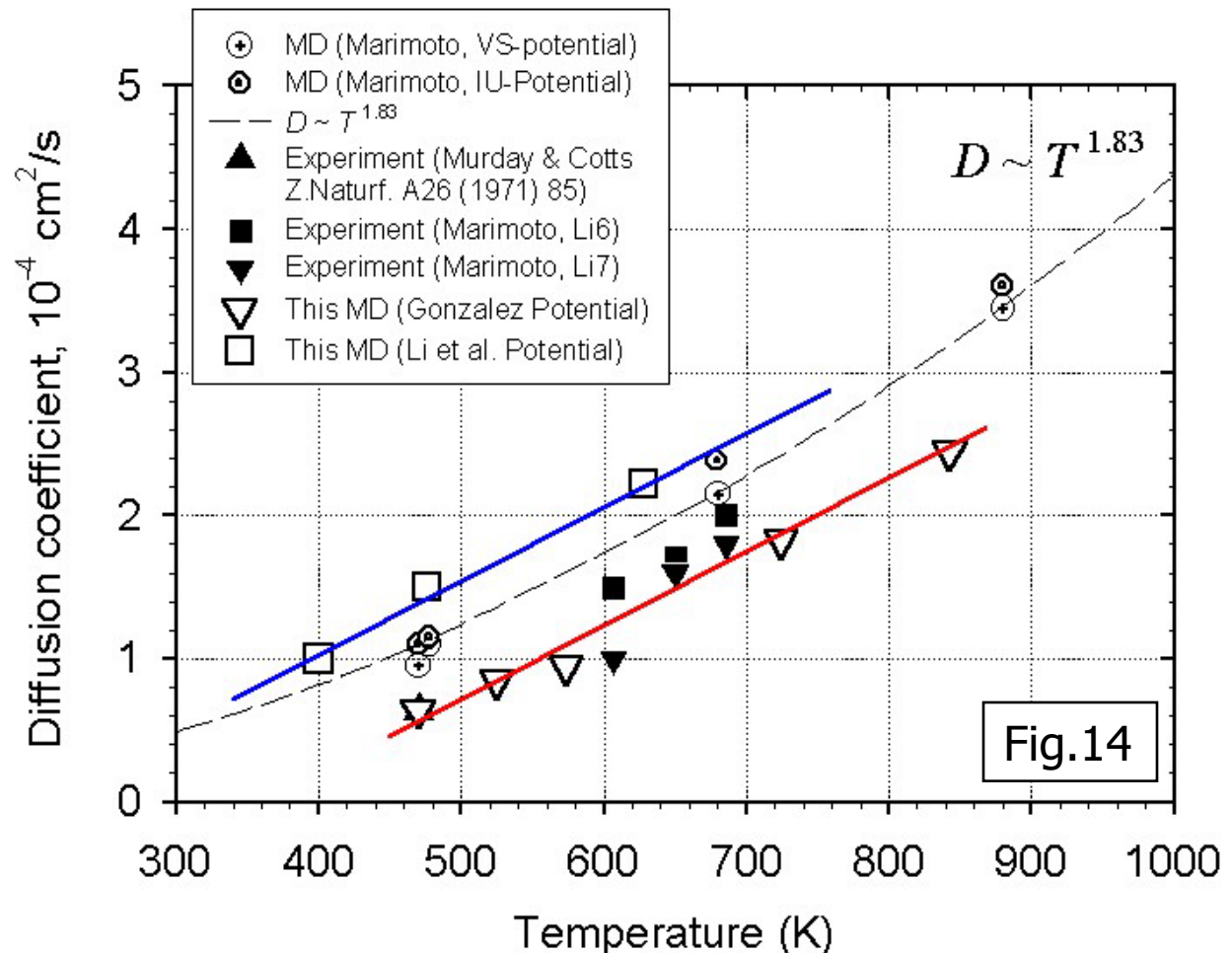Fig.12-13. The red lines are the trajectories for Lithium ions

Comparison with experiment

Here we compare the diffusion coefficients obtained by MD with experimental data. The red line is drawn as "an eye guide" for Canales's potential [1], the blue line – for the potential from Ref. [2] (Li et al.).
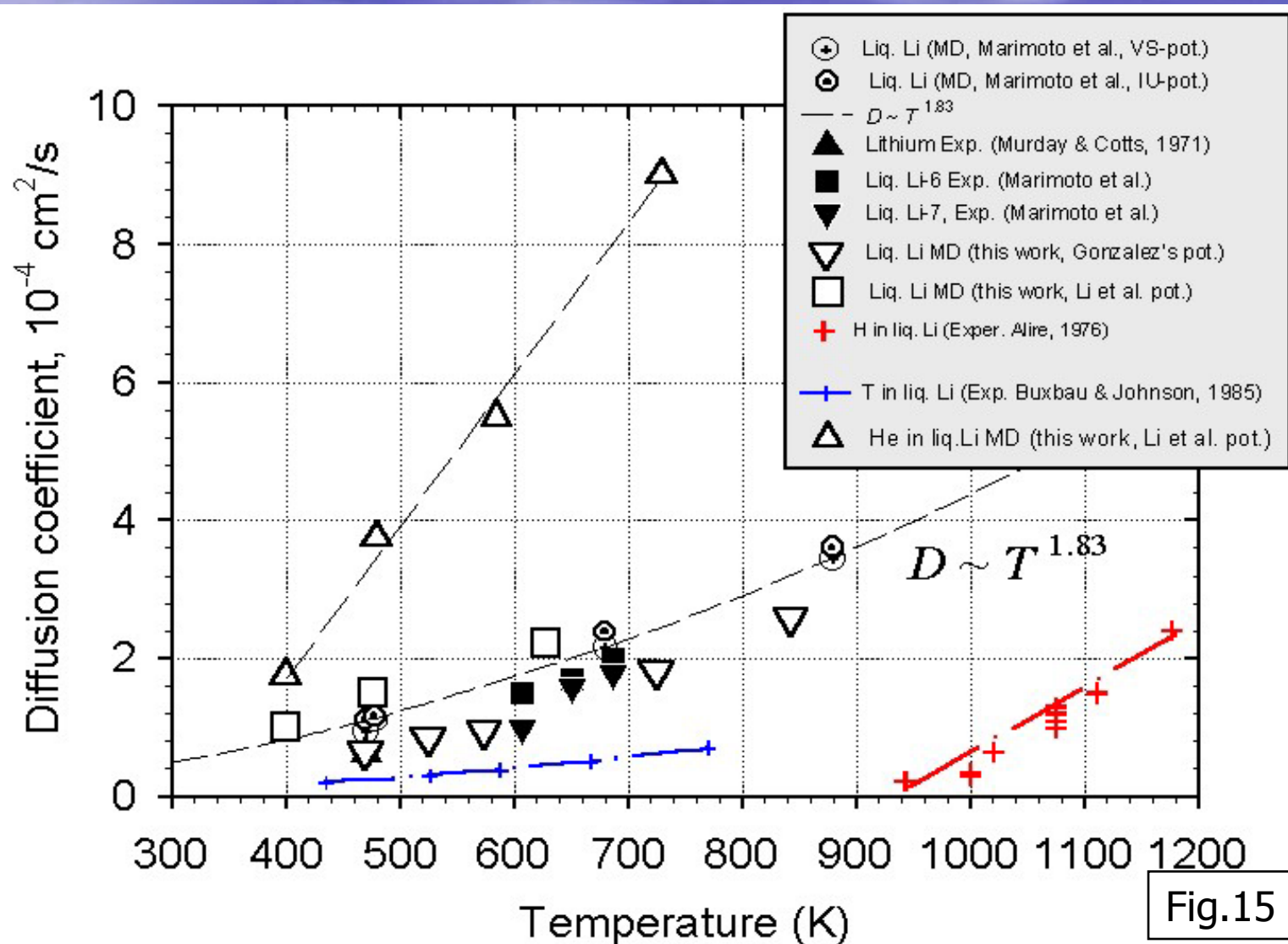
References:

[1]. M.Canales, L.E.Gonzalez, J.A.Padro, Phys.Rev. E50 (1994) pp.3656-3669.
[2]. Y. Li, E. Blaisten-Barojas, D.A. Papaconstantopoulos Phys. Rev. B57 (1998) pp.15519-15532.

Dependence of the self-diffusion coefficient in liquid Lithium on temperature

Legend:
- ⊕ MD (Marimoto, VS-potential)
- ◉ MD (Marimoto, IU-Potential)
- – – $D \sim T^{1.83}$
- ▲ Experiment (Murday & Cotts Z.Naturf. A26 (1971) 85)
- ■ Experiment (Marimoto, Li6)
- ▼ Experiment (Marimoto, Li7)
- ▽ This MD (Gonzalez Potential)
- □ This MD (Li et al. Potential)

$D \sim T^{1.83}$

Fig.14

He, H and T diffusivity in liquid Lithium

Fig.15

Proposal for MD simulation of bubble formation, blistering and sputtering of liquid Lithium

The formation hydrogen bubbles (blistering) in a metal target is well known in nuclear engineering [1]. However, an initial stage of bubble formation takes a long time compared to a typical MD-time scale, $\sim 10^{-9}$ sec.

Therefore, we plan to separate this task to two processes, with different time scales:

1. Slow process – formation of a critical nucleus.

This process could be studied by the kinetic theory balance equations [2]. However, for using this theory, we would need all the kinetic association and dissociation coefficients that should be obtained from experiment or calculated by Molecular Dynamics. The number of kinetic coefficients could be reduced by using the scaling theory. Still, this would be a huge computation task.

2. Fast process – Bubble collapse and sputtering.

This part is easy to model by Molecular Dynamics. As a first step, we plan to initiate MD simulations of a collapsing hydrogen and helium bubble or cavity, in a simple Lennard-Jones (LJ) liquid to speed-up the simulation. A series of MD simulations will be carried out with periodic boundary conditions using a cubic box containing up to 10^6 LJ particles to create initially an equilibrium bulk liquid.

The next step will involve a real ion-ion potential for liquid Lithium which is slower than a simple LJ-liquid because of long-range inter-ionic potential functions.

References:
[1].T.Vernhaus et al., Journal of Nuclear Materials, 290-293 (2001) pp.505-508.
[2]. Kinetic Theory of Liquids, Ya. Frenkel, Claredon Press, Oxford.

Hybrid Molecular Dynamics for sputtering yield calculation

Fig.16

Fig.17
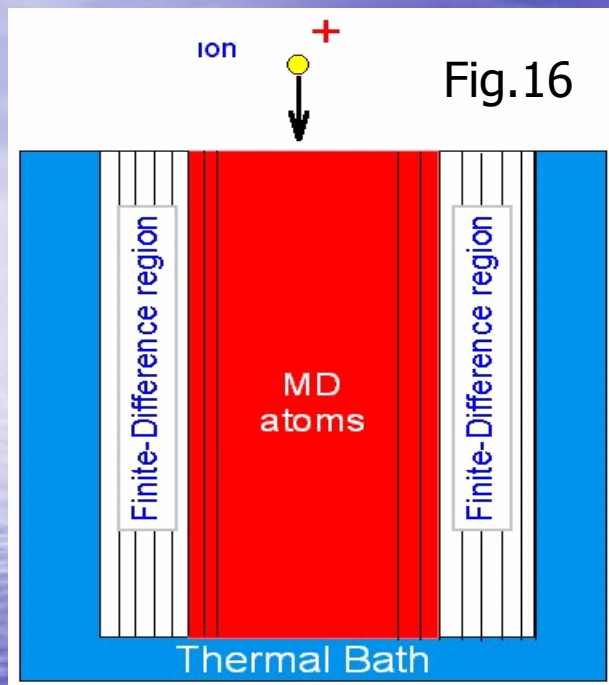
Our hybrid MD method combines conventional atomistic Molecular Dynamics (the red area in Fig.16) with a continuum mechanics (blue & white areas) equations solved by finite-difference technique.

1. Our HMD method demonstrates correct physics.
2. Additionally, it accelerates computation by a factor of 100.
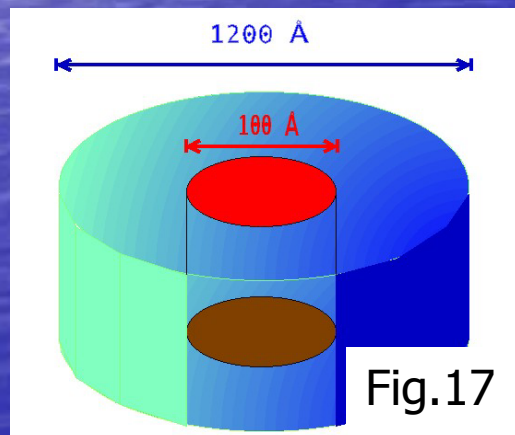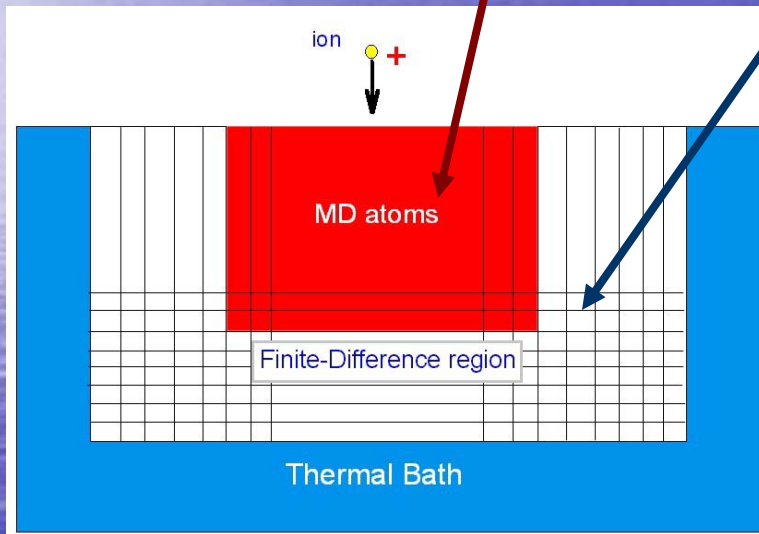3. It has almost no limitation for the outer system size.

Fig. 17 shows an example for sputtering yield calculation: the MD area (with extensive calculation load) is 100A in diameter, and the total diameter of the actual system is 12 times bigger. The effective size is 144 times bigger.

The MD region :

$$\ddot{\vec{r}}_i(t) = -\frac{1}{m}\sum_{j\neq i}\frac{\partial U_{ij}}{\partial \vec{r}_{ij}}$$

ion

+

MD atoms

Finite-Difference region

Thermal Bath

The Finite - Difference Region (Mesh) :

Thermal balance :

$$\frac{dT(\vec{r},t)}{dt} = \chi\,\Delta T(\vec{r},t)$$

The eq. of motion :

$$\frac{d^2\vec{u}_i}{dt^2} = \frac{\partial \sigma_{ik}}{dx_k}$$

χ – thermal diffusivit y,
K – bulk modulus,
ξ - bulk visco sity,
α – therm. expans. coeff,
μ - shear modulus,
η - shear visc osity.

$$\sigma_{ik} = -\alpha K T\,\delta_{ik} + K\varepsilon_{ll}\delta_{ik} + 2\mu\left(\varepsilon_{ik} - \varepsilon_{ll}\frac{\delta_{ik}}{3}\right)$$

$$+ \xi\varepsilon_{ll}\delta_{ik} + 2\eta\left(\dot{\varepsilon}_{ik} - \dot{\varepsilon}_{ll}\frac{\delta_{ik}}{3}\right)$$

$$\varepsilon_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{dx_k} + \frac{\partial u_k}{dx_i}\right)$$

This slide explains our Multi-scale Molecular Dynamics. For the MD region, the classical equations of motion are solved (the pink frame). The figure below the pink frame is a schematic of the system. The red area represents the area that is treated by conventional MD. The blue area is a thermostat at a constant (room) temperature. The white area (green frame) is for the finite-difference model that work very fast and extends the range of our model far beyond the typical MD models.

Summary

- Our MD simulations of liquid Lithium, with two interaction potentials give a good comparison with experiment for the Li self-diffusion coefficient ($\sim 10^{-4}$ cm2/s), obtained with Canales et al. potential. The potential suggested by Li et al. gives a diffusion coefficient almost twice as higher than experiment.

- We have computed the He diffusion coefficient in liquid lithium.

- We propose our future planning for an extensive Molecular Dynamics calculations of Helium and Hydrogen bubble formation in a liquid Lithium, an analog of blistering for a solid target, the following bubble burst and Lithium sputtering.